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Canaigre Investigations

VIII. Preparation of Tanning Extracts by Continuous Countercurrent Extraction*

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Previous papers from this Laboratory have reported the progress made in developing a domestic source of tanning extract from roots of canaigre (*Rumex hymenosepalus* Torr.). This paper, reporting further developments, describes several possible processes for the commercial production of tanning extracts from canaigre, in all of which continuous countercurrent extraction is used for separating the tannin from the roots. The economics of these various processes have not been thoroughly investigated as yet, and the qualities of the extracts produced have not been completely evaluated. Laboratory tests have shown, however, that at least one of these processes produces tanning extracts which could replace several vegetable tanning extracts in commercial use in this country.

The background of the canaigre project has been covered thoroughly in articles by Frey and Sievers [1] and Rogers and Russell [2]. The major difficulties in the extraction of canaigre are caused by the starch it contains. If the material is heated to a temperature at which the starch gelatinizes with water, the tannin becomes much more difficult to extract and, in addition, the liquors are much more difficult to clarify. Any process to extract tannin from canaigre must take these factors into consideration.

There are at least two strains of the canaigre plant, one having a root with a yellow interior and the other a root with a reddish interior. Since the latter is much higher in tannin content and purity, and since this strain is more easily extracted and gives liquors which are more easily clarified, reddish roots with a tannin content of about 37 per cent and a purity of about 67 were used in practically all these experiments.

Extraction of Tannin from Canaigre

Before the production of tanning extract from canaigre as an integrated process is discussed, it might be well to describe the extraction step, because the solvents and conditions used in the extraction influence the later steps of the process.

Previously an attempt had been made to leach canaigre in the conventional way used for tannin-bearing barks and woods, that is, percolating hot water through a stationary bed of shredded canaigre. It soon became apparent that the hot water gelatinized the starch, making the bed impermeable and the tannin difficult to extract. Cooler water improved the permeability of the bed slightly, but reduced the extraction efficiency materially because the shreds had to be large to permit the water to percolate through the bed. Beebe, Cordon and Rogers [3, 4] published the results of laboratory and small-scale work on a centrifugal filtration method of extraction with water. Although this worked well in the laboratory, when this method was extended to pilot-plant scale, the rate of filtration through a perforate bowl was rather slow. Centrifugal separation with a solid bowl was not thoroughly investigated because other means of processing appeared to be less costly. Accordingly, a vibrating screen and continuous rotary press of the conical type were substituted for the centrifugal filter. This method did not give quite as high extraction efficiencies as that previously mentioned mainly because considerable tannin was lost in fines, which were carried into the head liquor. The equipment and labor costs of handling both liquids and solids in this manner in a countercurrent batch operation on a large scale would be unduly great.

Luvisi and Rogers[5] and Luvisi, Cordon, Beebe and Rogers [6] have published results of laboratory-scale extraction of canaigre with organic solvent-water solutions, particularly acetone-water solutions. The present authors, in extending these studies to pilot-scale operations, have used isopropyl alcohol instead of acetone in most cases because it can be used in more dilute solution and because it is more feasible for commercial operations. The stationary vat leaching of large shreds of canaigre with dilute organic solvents instead of water was tried by Rieder et al [7]. The solvent improved the permeability of the bed, and uniform shreds relatively free of fines made it even more satisfactory. But even though the recovery of tannin was increased somewhat over that obtained by water extraction, it still was not enough to make this process commercially feasible. The continuous countercurrent extraction methods presented in this article are the result of attempts to make the process less expensive.

Before the study was started, a survey was made of the equipment used in the solvent extraction field. The common types are (1) the basket or paternoster type and a horizontal development of this called the Rotocel, (2) the vertical-column tray type, (3) screw or Redler conveyors, and (4) the paddle-wheel type or Kennedy extractor. The only one definitely unsuitable was the basket type, since it depends on percolation of the solvent through a stationary bed of fine material in a short time. As we had proved previously, this can not be done with canaigre because it swells and becomes impervious to the solvent. Any of the other types of extractors might be satisfactory for the purpose, but since a Kennedy extractor was available at the Laboratory it was used for this work.

The Kennedy extractor (Figures 1 and 2) consists of a long narrow horizontal chamber having a jacketed bottom made up of a series of semicylindrical cells. In each cell is a paddle wheel or rotor with four perforated blades turning slowly in such a way that the solids are propelled along the extractor. As modified from the original design, the extractor used now has perforated weirs between the cells and a scraper blade on each paddle wheel to scrape the solids off the paddle wheel into the next cell. The solids are metered into one end of the extractor by a grooved disk feeder, and removed at the other end by a drag conveyor. The solvent is fed by a positive displacement metering pump through a rotameter into the last cell before the drag conveyor, and by a slight slope of the extractor is caused to flow in a direction countercurrent to that of the solids. It is discharged as head liquor at the opposite end of the extractor. The extractor has 14 extraction cells and 1 filter cell, but it is adaptable so that fewer can be used if desired.

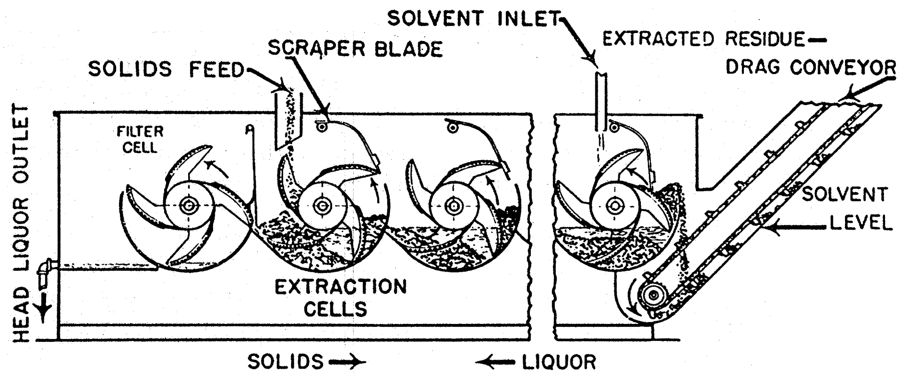


Figure I. Sectional View of Kennedy Continuous Countercurrent Extractor

A series of experimental runs was made in which the solvents were (1) distilled water, (2) an aqueous solution containing 18 per cent by volume of isopropyl alcohol and (3) another aqueous solution containing 25 per cent by volume of acetone. Other variables studied were the method of cutting and the size of the solids, retention time, liquid-to-solids ratio, number of cells necessary for the extraction and temperature of the solvent. In all cases, moisture analyses were made on the solids as fed and on the spent marc, and tannin analyses were made on the solid feed, the spent marc and the head liquor. The samples of fresh and spent materials were extracted for analysis by an improved procedure,[5] and all the solutions and liquors were analyzed for tannin by the official methods of the A.L.C.A.[8]. The details of these 52 runs are the subject of a paper devoted solely to extraction[9], but we shall summarize the conclusions.

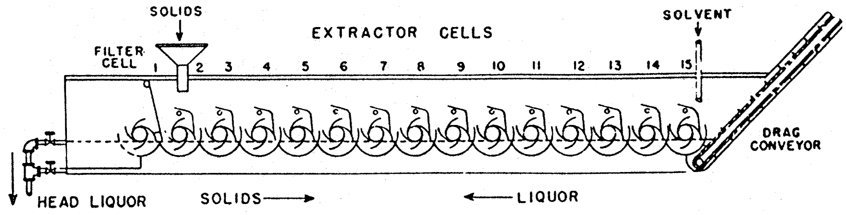


FIGURE 2. DIAGRAM OF KENNEDY CONTINUOUS COUNTERCURRENT EXTRACTOR

1. *Preparation of roots*: For extraction with aqueous organic solvents, the dried roots were ground in a rotary knife cutter (Ball and Jewell type) with a 1/8 inch screen, the ground material was passed over a 20-mesh screen, and the material held on the screen was reground. This preparation gives good extraction and a minimum amount of fines in the head liquor. For water extraction, the dried roots were ground in the rotary knife cutter with a 1/16 inch screen. Although this preparation causes somewhat more fines to be carried into the head liquor, the finer comminution is necessary for water extraction. Other methods of grinding might produce even a better preparation for extraction.

2. *Retention time of the solids in the extractor*: Retention times of 60 to 150 minutes were investigated. It was concluded that for extraction with aqueous organic solvents, a retention time of 90 minutes was most practical, but for extraction with water a retention time of 120 minutes was better.

3. *Liquid-to-solids ratio*: With dilute organic solvents a liquid-to-solids ratio of 10 to 1 gave about as good an extraction as could be attained. With water, slightly higher ratios might be more economical.

4. *Number of cells required*: For extraction with dilute organic solvents, only 10 Kennedy cells were useful. With water as the solvent, extraction takes place in all 14 cells.

5. *Effect of different solvents and of temperature*: With 18 per cent by volume aqueous isopropyl alcohol at 112° F. and 25 per cent by volume aqueous acetone at room temperature, 94 per cent of the tannin was recovered in the head liquor of the Kennedy extractor under the optimum conditions described. Although 25 per cent acetone gave tannin recoveries higher by about 1 to 2 per cent than those given by the 18 per cent alcohol, it is believed that the use of this solvent on a commercial scale would be undesirable because of the difficulties and expense involved in handling this more inflammable material. Increase in temperature of the acetone had little if any beneficial effect. The effect of increasing the temperature of the isopropyl alcohol above 112°

F. has not been thoroughly investigated. Below 112°F., however, the extractive powers of this solvent decrease appreciably.

With water at 112°F. as the extractant, 73 per cent of the tannin was recovered. At elevated temperatures, recoveries up to 78 per cent have been reached. These values cannot be compared with those of Beebe et. al.[3, 4] because the present figures are based on the improved analyses of the roots by the Luvisi method[5]. If the earlier investigations had been based on this improved analytical procedure, the recoveries of tannin they reported would have been somewhat lower.

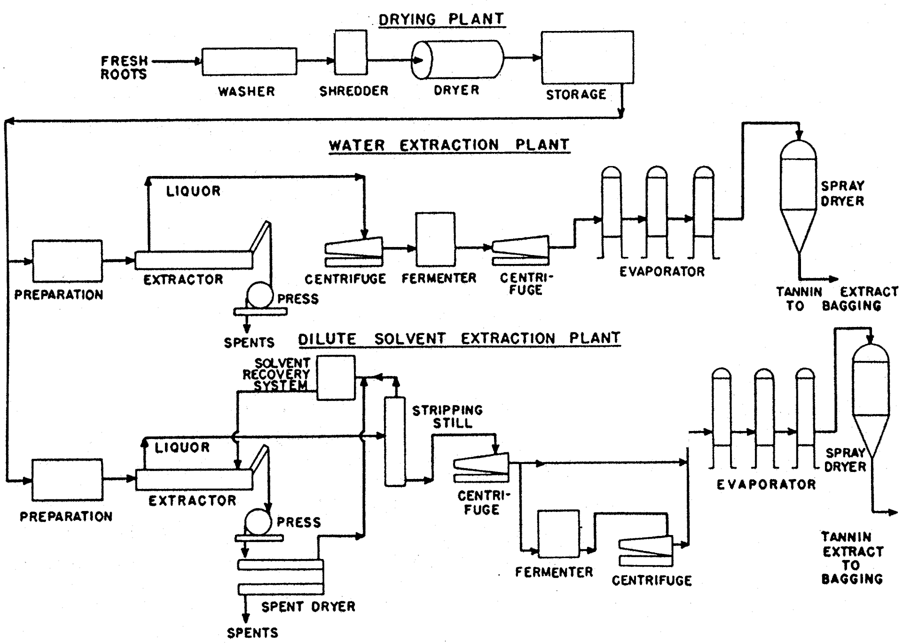
Because these solvents give greater recovery of tannin it might appear that extraction with organic solvents would be the best process to use commercially. But recovery is not the complete picture. The quality of the tanning extract produced and many economic factors must be considered. The tanning quality of extracts prepared with different solvents and at different temperatures is discussed in a paper presented by Beebe et al. at the meeting of the American Leather Chemists Association, French Lick, Ind., May 31-June 2, 1950. The economics cannot be worked out accurately because of uncertainty regarding the price of the raw material in terms of tannin content and because the possibilities of utilizing the spent canaigre and other byproducts have not yet been determined. It must be remembered that if organic solvents are used, the effective solvent-recovery system required will cause additional expense. Before a definite commercial choice can be made, the economic aspects of the various processes must be thoroughly evaluated.

Production Process—Fresh Roots to Powdered Extract

We shall now discuss the over-all process from fresh roots to powdered tanning extract. It must be kept in mind that the choice between water and aqueous organic solvent will determine the character of the rest of the process. The flow sheets for the two processes are shown in Figure 3. The danger of iron contamination of tannin must be remembered; all piping and metal equipment that come in contact with the canaigre roots or the liquors should be copper, brass, or stainless steel.

Since it appears to be most economical to operate the extraction plant on a 12-month basis, and the canaigre harvesting season lasts only 3 months, the processes described here include shredding the roots and drying them for storage. Laboratory tests have shown that to keep the shredded roots from molding and fermenting they must be dried to a moisture content below 16 per cent[10]. Freshly harvested roots can be washed in any type of commercial potato or sugar beet washer. The choice of a shredder depends on the drying method. Preliminary drying investigations have indicated that canaigre can be satisfactorily dried in either of two ways. Cut into shreds

FIGURE 3
FLOW SHEETS FOR RECOVERY OF TANNING EXTRACTS FROM CANAIGRE ROOTS



they can be dried in a belt dryer in which air at 150° F. is blown down through a thin bed of shreds. Or, ground in a rotary knife cutter or sharp knife hammer mill equipped with a ¼-inch or ½-inch screen, they can be dried in a parallel current rotary kiln dryer with air at 500 to 600° F. inlet temperature. The latter drying method, of course, is less expensive; for Kennedy extraction wotk it produces a very satisfactory product.

When water is used as the extractant, the spent material trom the extractor is passed through a press and the press liquor is returned to the extractor with the fresh solvent. The pressed spent roots do not have to be dried. Because of their high starch content, they might find various uses.

The water extract is passed through a centrifuge, which decreases the insoluble material to 2 or 3 per cent of the total solids in the clarified liquor. After centrifuging, the water-extracted liquor, which has a purity of about 50, is sterilized by heating to 200° F., cooled to 87° F. and fermented to remove the sugars, thereby increasing the purity. This fermentation was developed by Cordon, Beebe and Rogers [11]. They used an *Aerobacter aerogenes* (designated as WH), which ferments the sugars in tannin liquors in about 16 hours, producing mainly 2,3-butanediol, and smaller quantities of acetoin, ethanol, and organic acids [12]. By this operation, the purities of water-extracted liquors can be increased to 60 or 70. After fermentation, the liquors are recentrifuged to remove insolubles produced during this step.

The clarified liquors are transferred to a standard multiple-effect evaporator, and concentrated either to a liquid extract of about 60 per cent solids or to a liquid having a solids content suitable for spray drying. Spray drying has been successfully accomplished with canaigre extracts ranging from 25 to 50 per cent in solids content and with inlet air temperatures of 400 to 600°F.

When dilute organic solvents are used, the following modifications must be made in the process just described for water extraction. The pressed spent roots must be dried to recover the valuable solvent. Before the head liquor from the extractor is centrifuged, it must be passed through a stripping still to recover the solvent. It has been calculated and demonstrated that if 18 per cent by volume of aqueous isopropyl alcohol is used as the extractant, when two-fifths of the solution has been vaporized, the distillate will contain all the alcohol at a concentration of about 40 per cent. This distillate can be diluted and recycled to the extraction system.

Since solvent-extracted liquors have a purity of 59 to 63, there is a question as to whether it is necessary to increase the purity by fermentation. Luvisi et al. [6] state that fermentation is not necessary. If fermentation is not used, the second centrifuging is eliminated.

The remainder of the process is the same as that for water-extracted liquors.

Production of Extracts for Tanning Tests

To produce a sufficient quantity of canaigre extract for tanning tests, several production runs were made on the Kennedy extractor with different solvents and conditions. The four solvents used were water, 10 per cent by volume aqueous isopropyl alcohol, 18 per cent by volume aqueous isopropyl alcohol, and 25 per cent by volume aqueous acetone. Four water runs were made, one each at temperatures of 114°, 150° and 170° F., and one in which the water was used at 175° at the solids discharge end of the extractor and cooled until it was 115° F. at the head liquor end. Table I gives the conditions, tannin recoveries, and analyses of the powdered extracts produced. The duration of the runs varied somewhat but averaged 24 hours. The roots used were a reddish strain having 37 per cent tannin content and a purity of 67; they had been dried in a belt dryer with air at 150° F. The dried roots were fed into the extractor at a rate of approximately 2.5 pounds per hour. The head liquors, which were not collected until the extractor had reached equilibrium, were carried through all the stages of the processes described above, including fermentation in every case except the run in which 25 per cent acetone was used.

Table I shows that the actual recovery of tannin in the head liquors for the water runs ranged from 62 to 71 per cent. For the 18 per cent isopropyl alcohol run, the recovery was 88 per cent, and for the 25 per cent acetone run, 86 per cent. Unfortunately, extraction data could not be obtained for the 10

TABLE I

Spray-Dried Canaigre Extracts Made for Tanning Tests

Conditions of Extraction					Head Liquor Produced		Spent Roots	Over-All Balances*		Analyses of Powdered Tanning Extracts					
Run No.	Solvent	Temp.°F.	Retention Time Min.	Liquid to Solids Ratio	Tannin Recovery %	Purity	Tannin Content %	Tannin %	Soluble Solids %	Total Solids %	Soluble Solids %	Insoluble Solids %	Non-tannin %	Tannin %	Purity**
CA31W47	Water	114	120	10.6	67	58.2	17.2	90	95	96.4	95.1	1.3	35.1	60.0	63.0
CA31W48	Water	150	90	10.8	71	57.5	15.5	89	93	96.0	92.3	3.7	28.9	63.4	68.7
CA31W45	Water	170	90	10.2	66	58.5	13.2	82	87	95.1	92.3	2.9	34.7	57.5	62.4
CA31W46	Water	175 cn spent roots to 115 on feed	90	13.1	62	57.4	15.4	82	86	96.1	94.0	2.1	33.2	60.8	64.7
CA31E45	10% Isopropyl alcohol	112	90	——	—	59.4	7.4	—	—	96.4	95.0	1.5	32.3	62.7	66.0
CA31E44	18% Isopropyl alcohol	112	90	11.1	88	62.5	5.8	95	100	96.9	93.9	3.0	28.7	65.3	69.5
CA31C3	25% Acetone	80	90	11.9	86	62.2	4.8	92	98	94.9	93.6	1.3	35.2	58.5	62.4**

*Over-all balances are calculated as the amount of the constituent recovered in the head liquor plus the amount in the spent roots divided by the quantity originally in the roots.

This value is expressed as percentage.

**The increase in purity shown in this column is the result of fermentation of the head liquors. All the liquors were fermented except that from Run C3.

per cent isopropyl run. It will be noticed that the tannin recoveries are not quite so high as those reported earlier in this paper as being attainable and also that the effect of increasing the temperature of the water on the extraction is not clearly shown by these results. The reasons for this are twofold. First, a certain deviation is allowable in any one run because of errors in experimental measurements and in analyses which are unavoidable in working with natural products. Second, the data reported are for a series of individual runs made solely to produce tannin for tanning tests. Because of the comparatively large quantities of tannin required, the extractor was operated overnight unattended which precluded the rigid controls used in our experimental work. It will be seen that the recovery figures in Table I which may be considered low are accompanied by low tannin balances and low soluble-solids balances, indicating inaccuracies in measuring or losses of material. The figures reported as conclusions in the earlier part of this paper are the results of a series of many experimental runs. The effect of increasing the temperature of water for extraction is indicated better by the column in Table I giving the tannin contents of the spent roots. These data show clearly that the higher the temperature of the water the less the amount of tannin in the spent roots.

Summary

A process has been presented for producing tanning extract from canaigre roots by continuous countercurrent extraction with various solvents. The process includes shredding and drying the fresh roots, preparing the dried material, extracting with water or with dilute aqueous solutions of organic solvents, stripping to recover solvent when necessary, centrifuging, fermenting if necessary, clarifying, concentrating and spray drying to powdered tanning extract. Details are reported of runs made to prepare sufficient tanning extract by each of these processes to permit evaluation of the quality of the tannin by tanning tests. Economic evaluation of these processes cannot yet be made because of the uncertainty of the price of the raw material in terms of tanning and because uses have not yet been found for the byproducts.

Acknowledgment

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